An Overview of Synchrotron X-ray Absorption Spectroscopy

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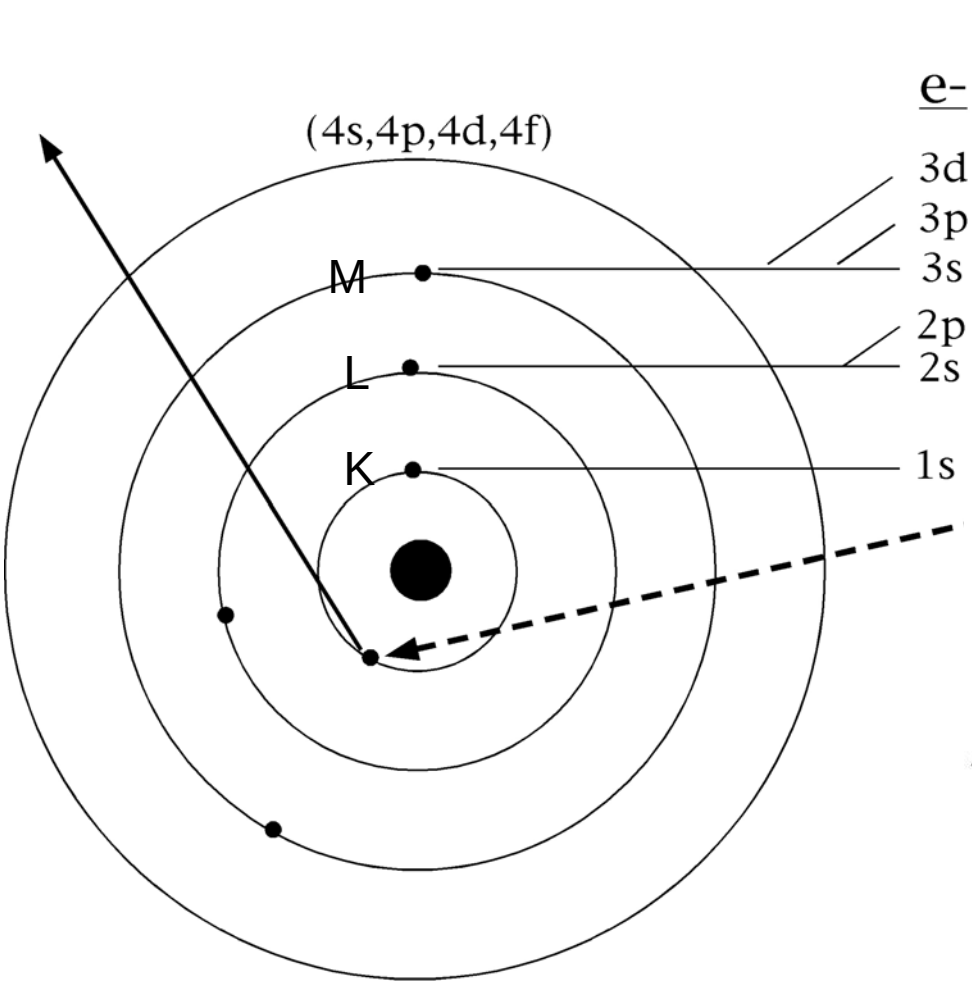
"Nothing is so difficult
but that it may be found out
by seeking."
-Terence (ca. 150 BC)

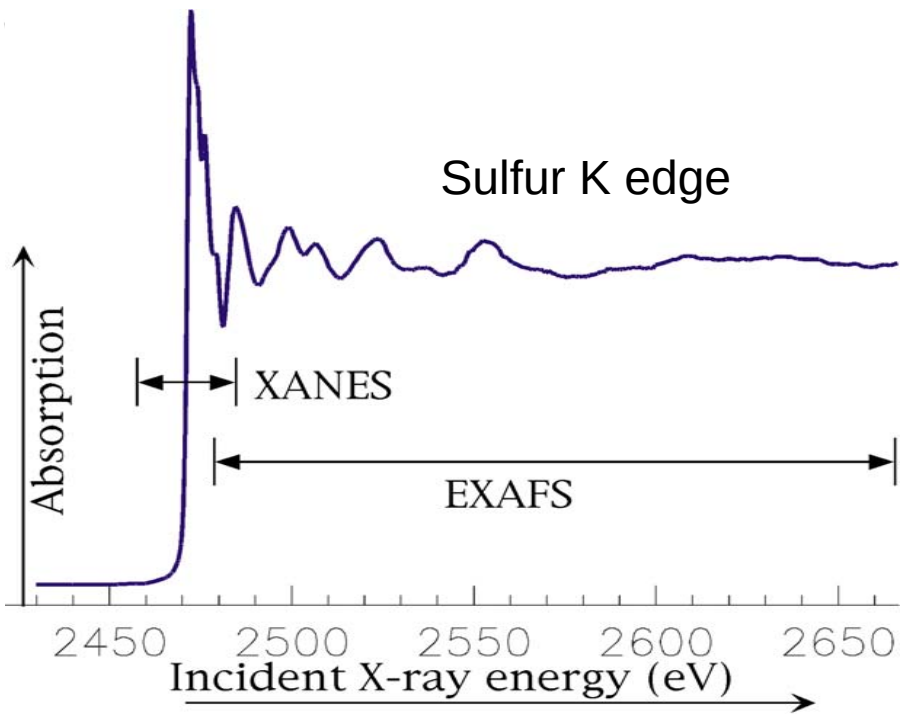
Applications of Synchrotron XAS

- A probe of chemical and structural state:
  - Oxidation state and chemical bonding
  - Local and short-range structures
- Element-specific and non-destructive
- Trace or major components, processes
- Applications to chemical, environmental, material and biological systems

Xray Absorption Spectroscopy:

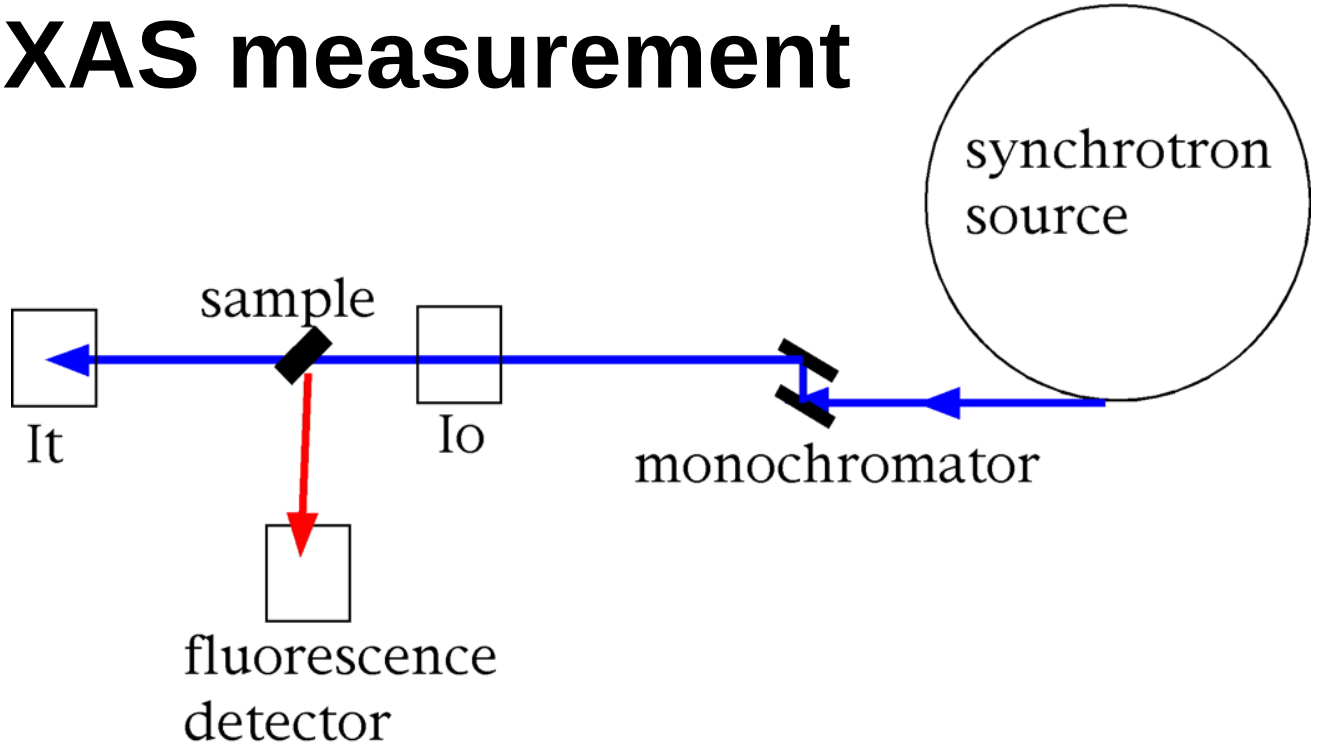


Each edge of each element has a characteristic binding energy



Absorption occurs when the energy of the incident photon is sufficient to eject the electron.

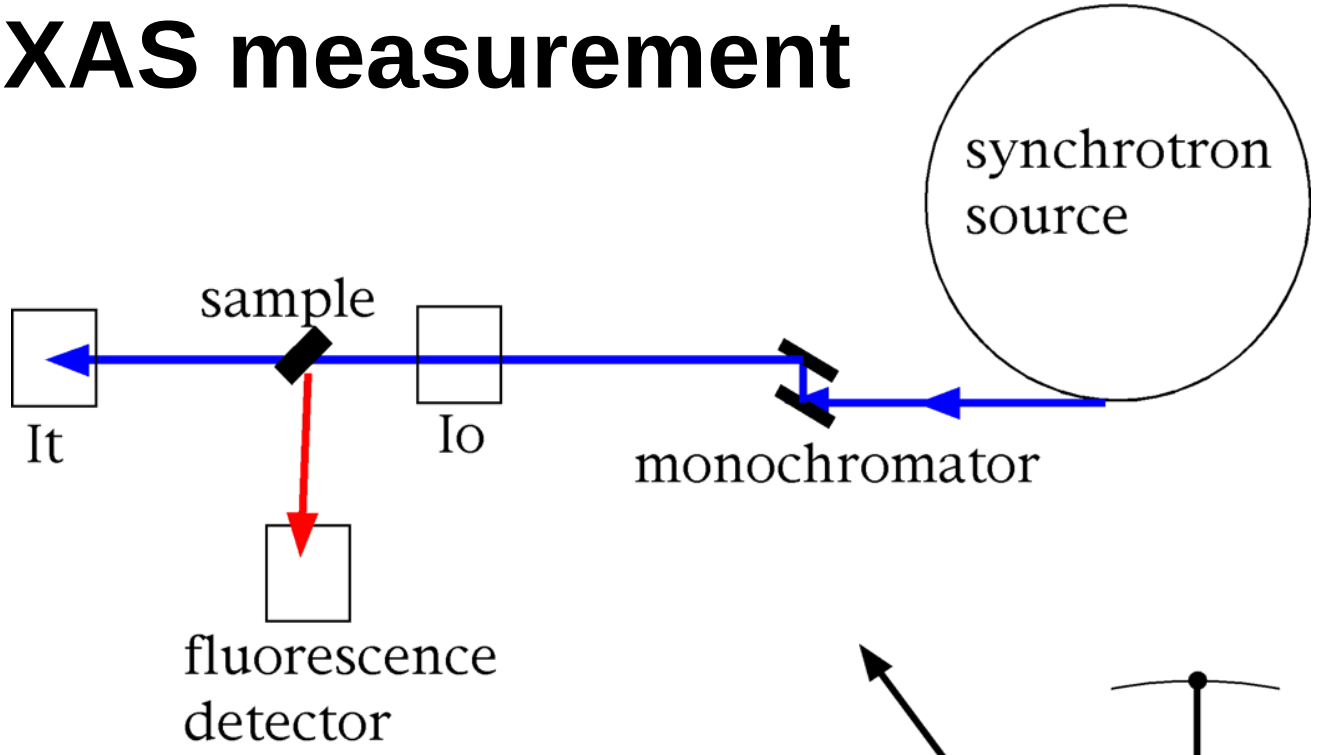
XAS measurement

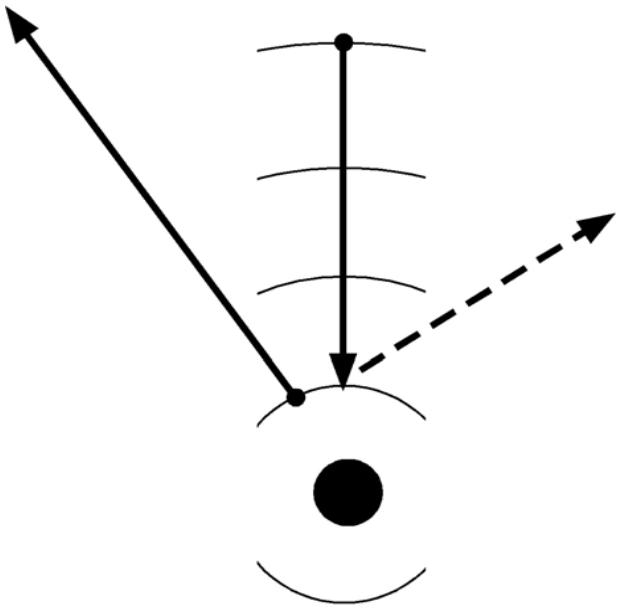


- **Direct**: transmission through sample.

$$\text{Absorption} = \ln(I_o/I_t)$$

XAS measurement

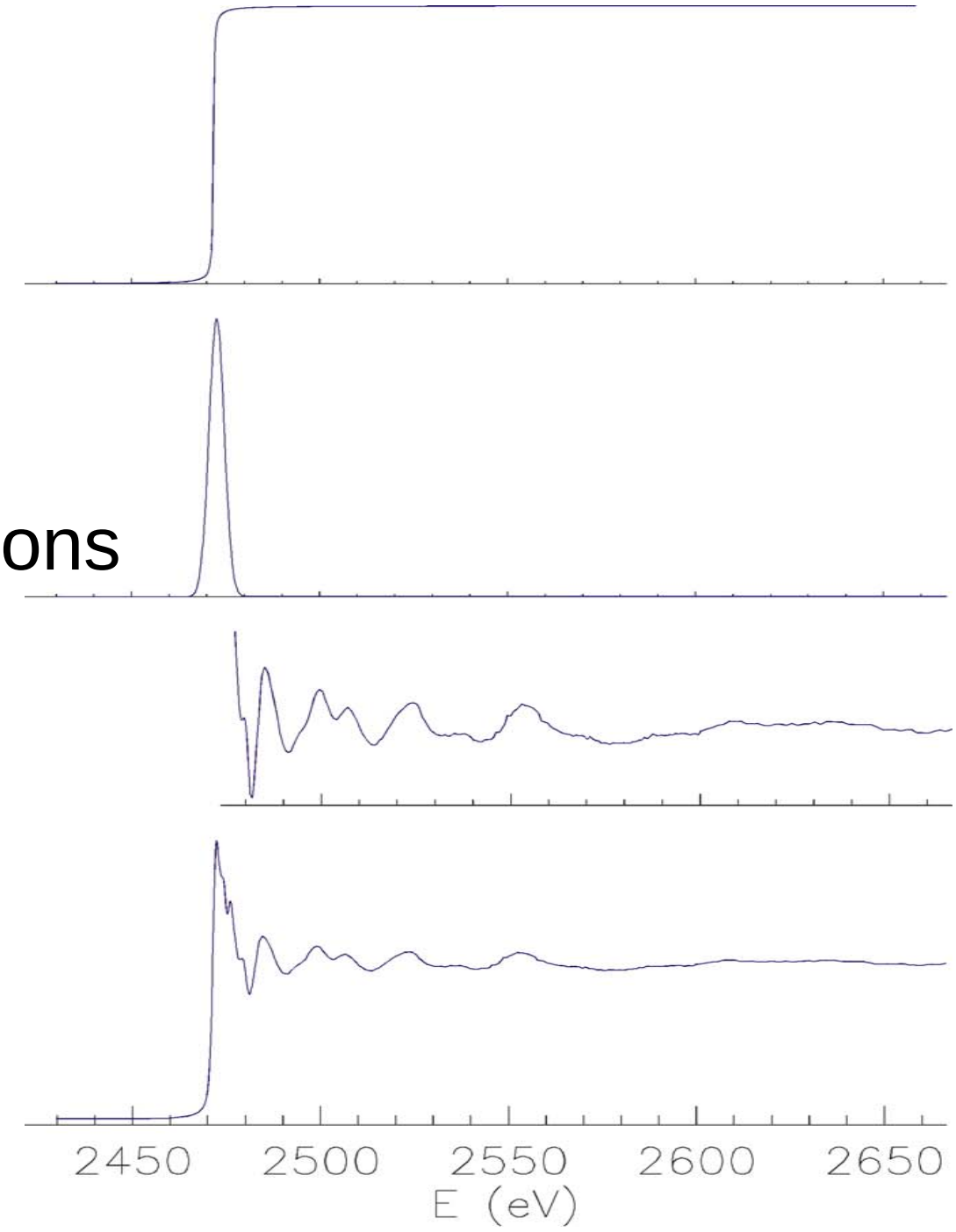




- **Indirect**: X-ray fluorescence produced as electron “hole” is filled.
- Characteristic energy for each element.
- Proportional to absorption.

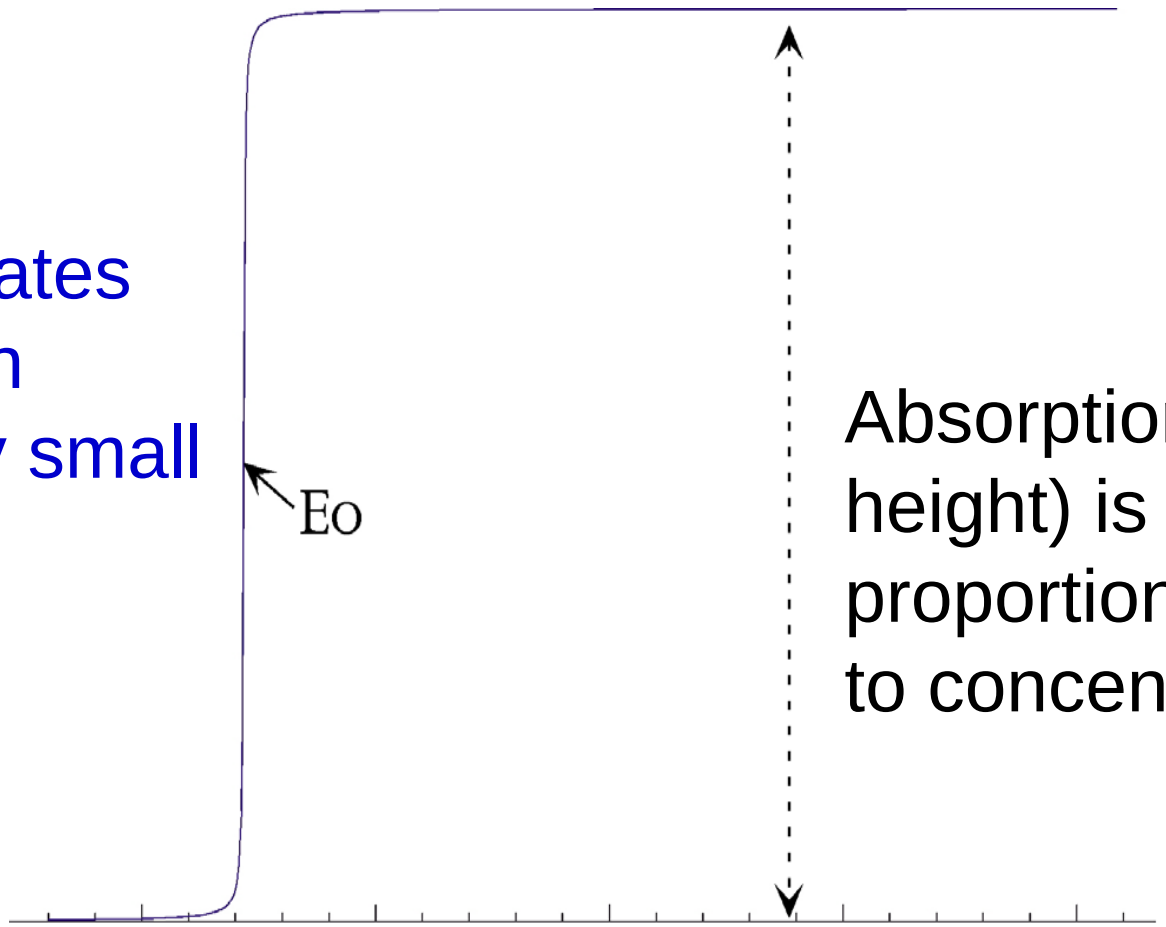
Three components of XAS:

- Edge step
- Electron transitions
- Extended oscillations
- Each carries different information.



Absorption edge step

Eo indicates oxidation state, by small shifts.

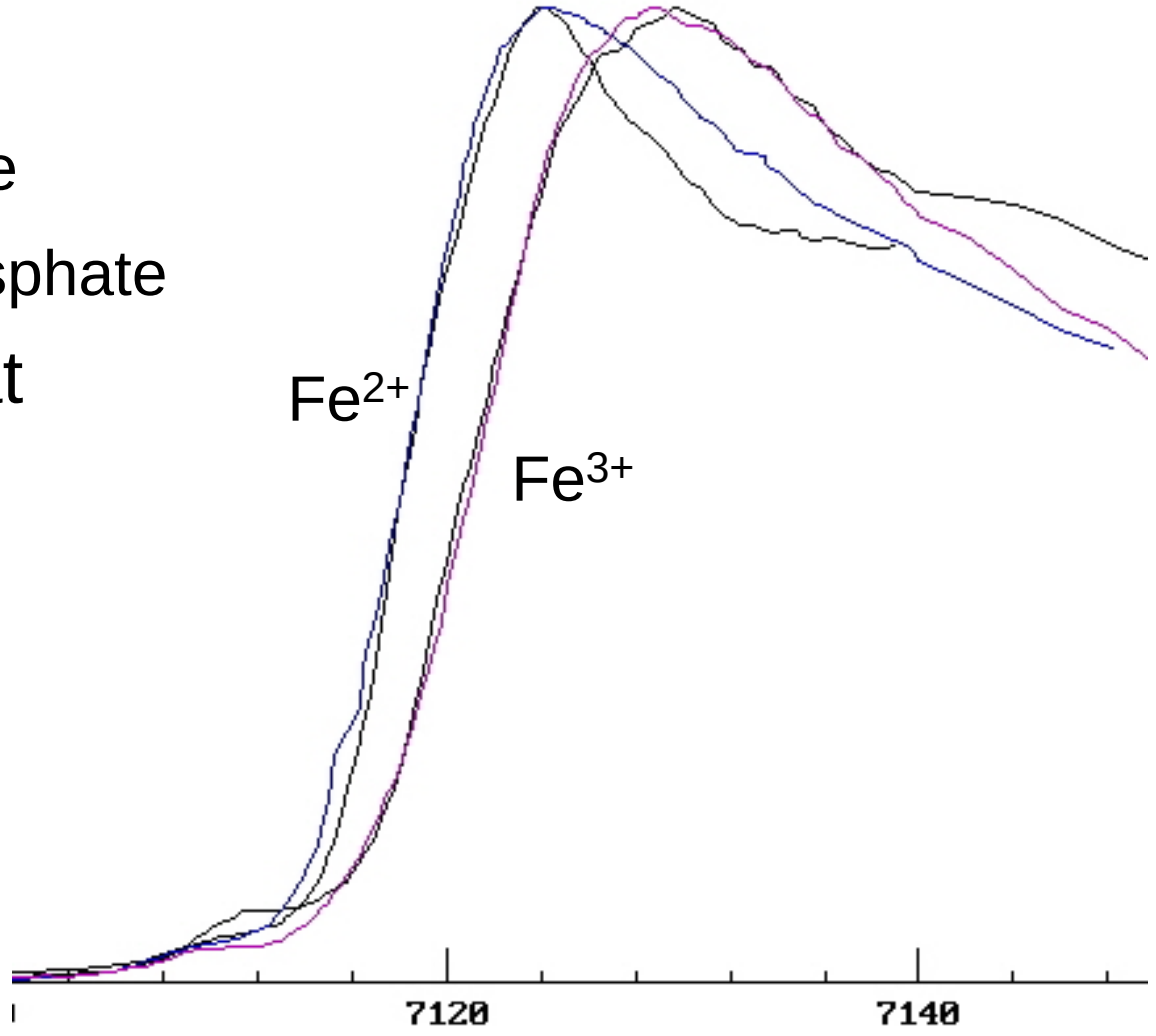


Absorption (step height) is proportional to concentration.

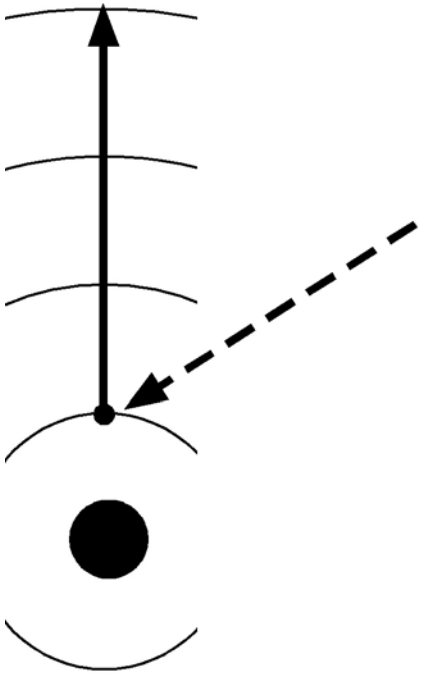
<<<<<reduced oxidized>>>>>

Fe K absorption edge

- Standards:
  - Hematite: Fe^{3+} oxide
  - Vivianite: Fe^{2+} phosphate
- Sediment samples at different depths
- Indicative of redox processes

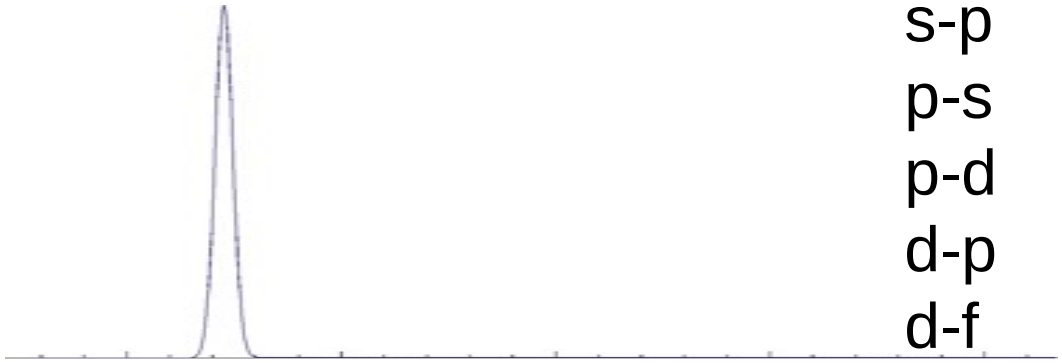


Electron transitions



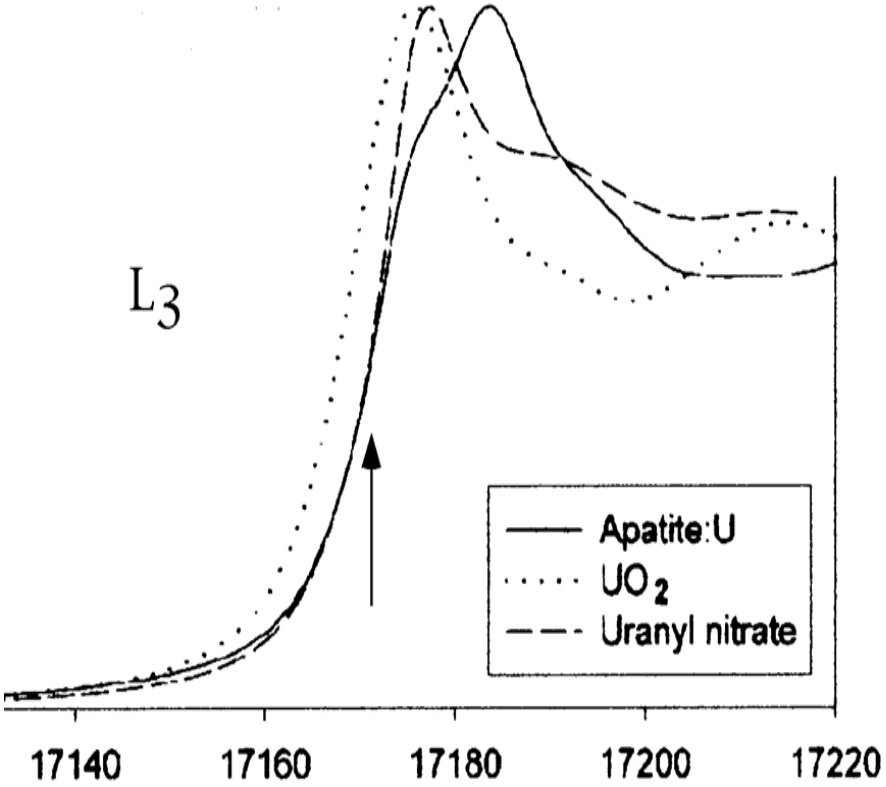
- Promotion of electron to available (unfilled) level of absorbing atom -- or neighbor.
- Peak energy differs from edge energy.
- Sensitive to electronic configuration and bonding.
- Rules:

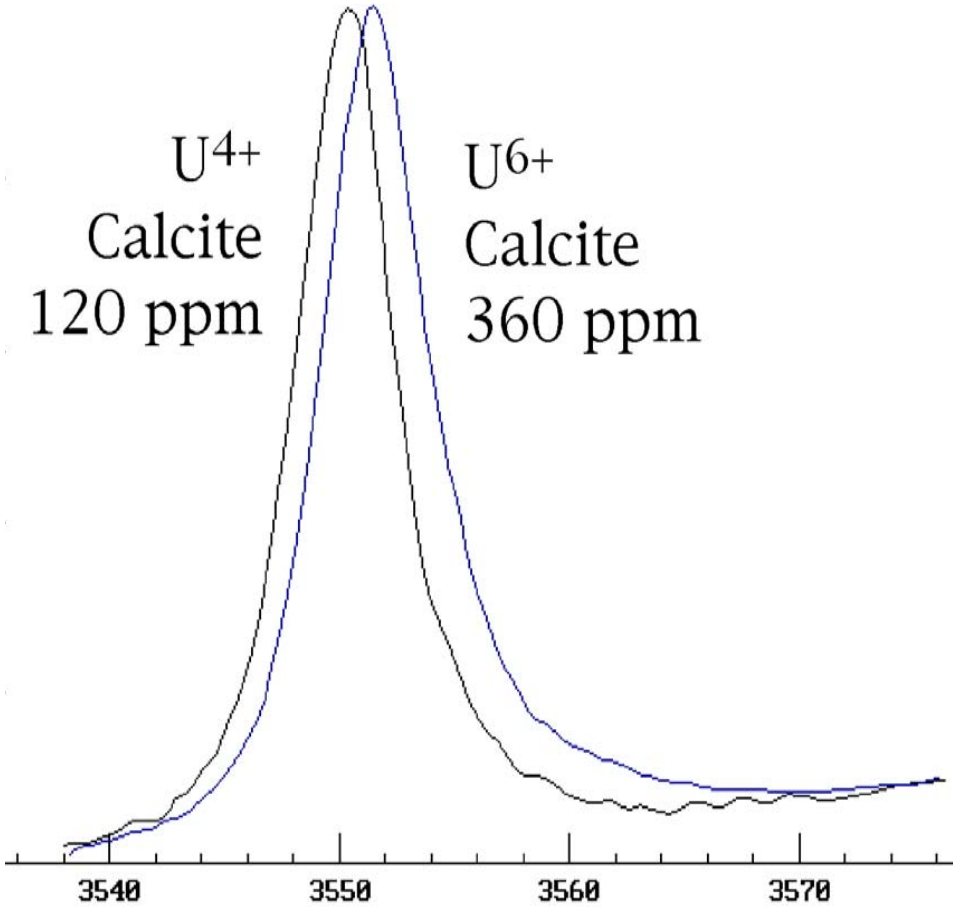
Allowed:	Forbidden:
s-p	s-s
p-s	p-p
p-d	d-d
d-p	
d-f	



Uranium L_3 and M_5 edges

- L_3 absorption edge indicates oxidation state
- M_5 edge dominated by 3d > 5f transition
- Importance: U^{6+} highly soluble, U^{4+} relatively immobile



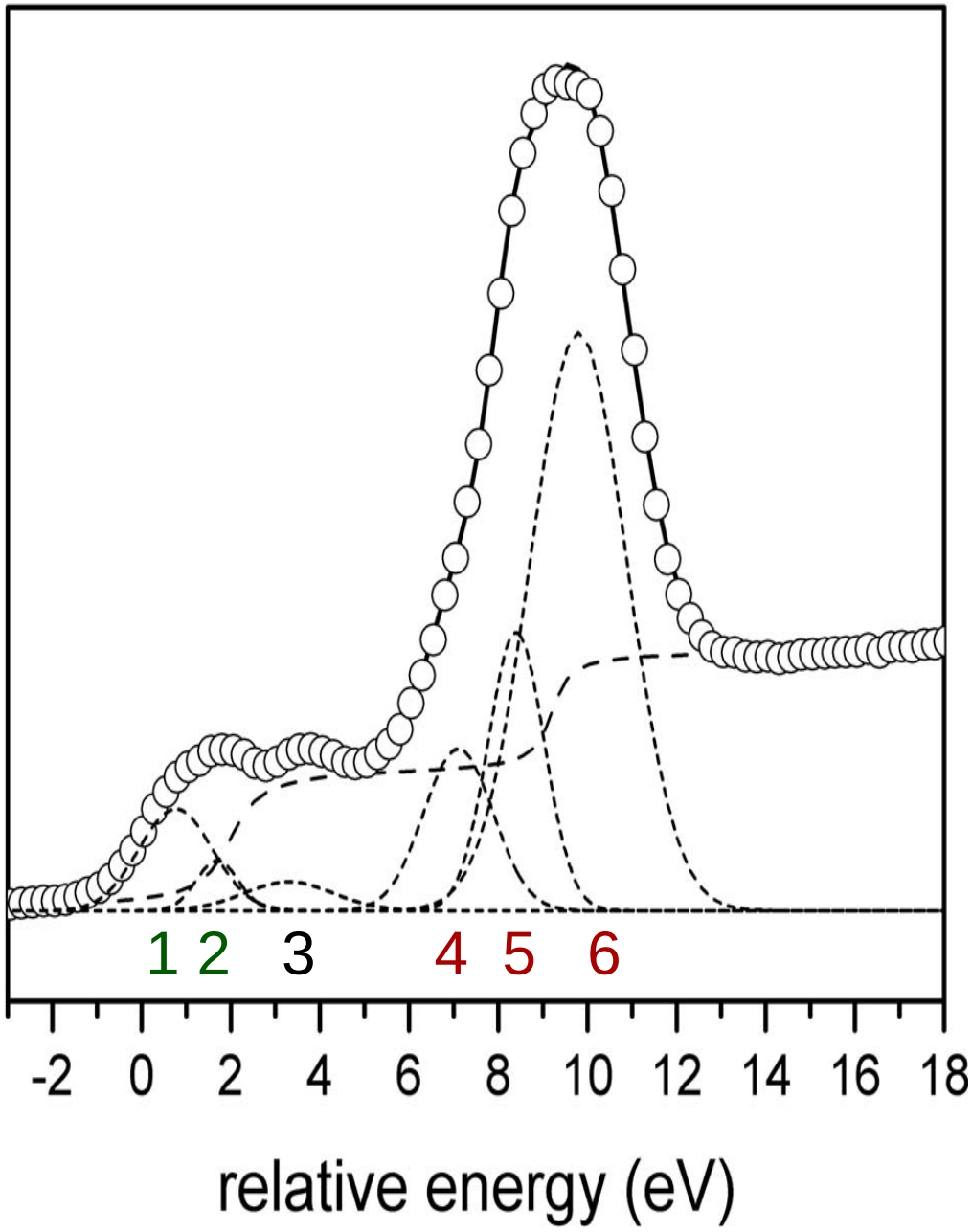


Rakovan et al

S K edge

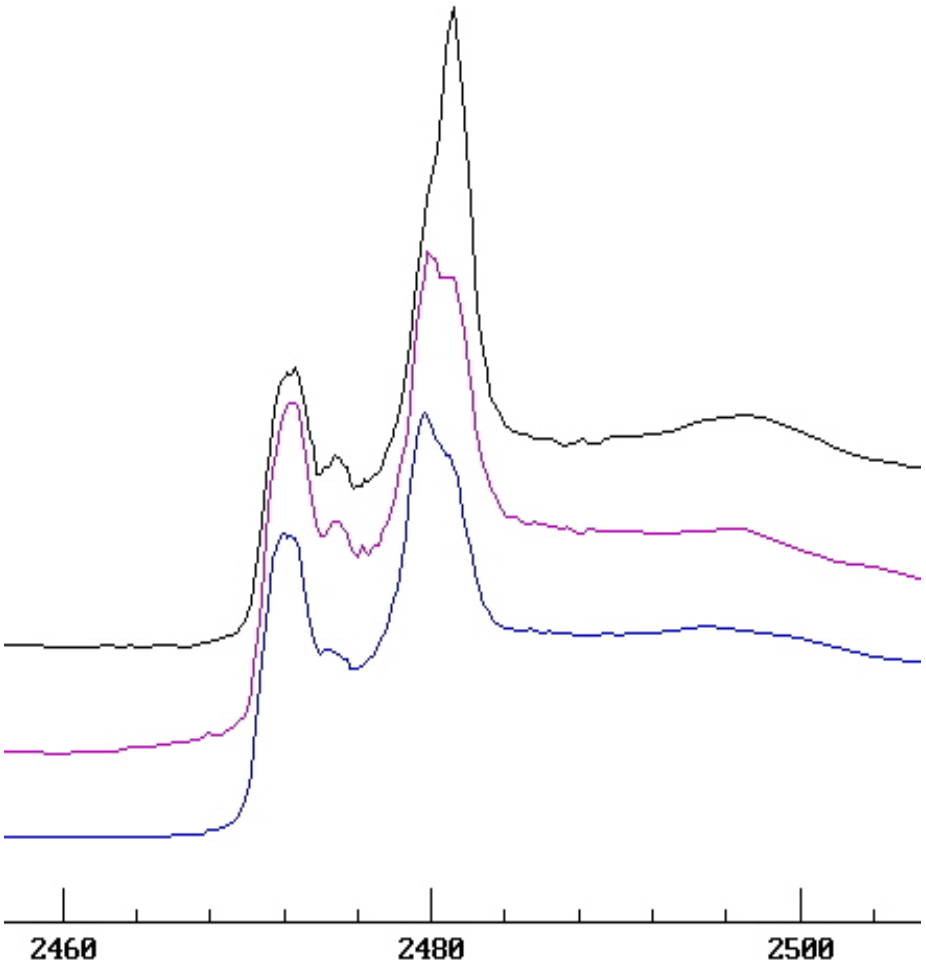
- 2 edge steps (oxidation states)
- 1s to 3p electron transition:

1: sulfide/thiol (R-S-R/R-SH),
2: thiophene,
3: sulfoxide (R-(SO)-R),
4: sulfite/sulfone ($R\text{-}OSO_2^-$/$R\text{-}(SO_2)\text{-}R$),
5: sulfonate ($R\text{-}SO_3^-$),
6: sulfate ester ($R\text{-}OSO_3^-$)

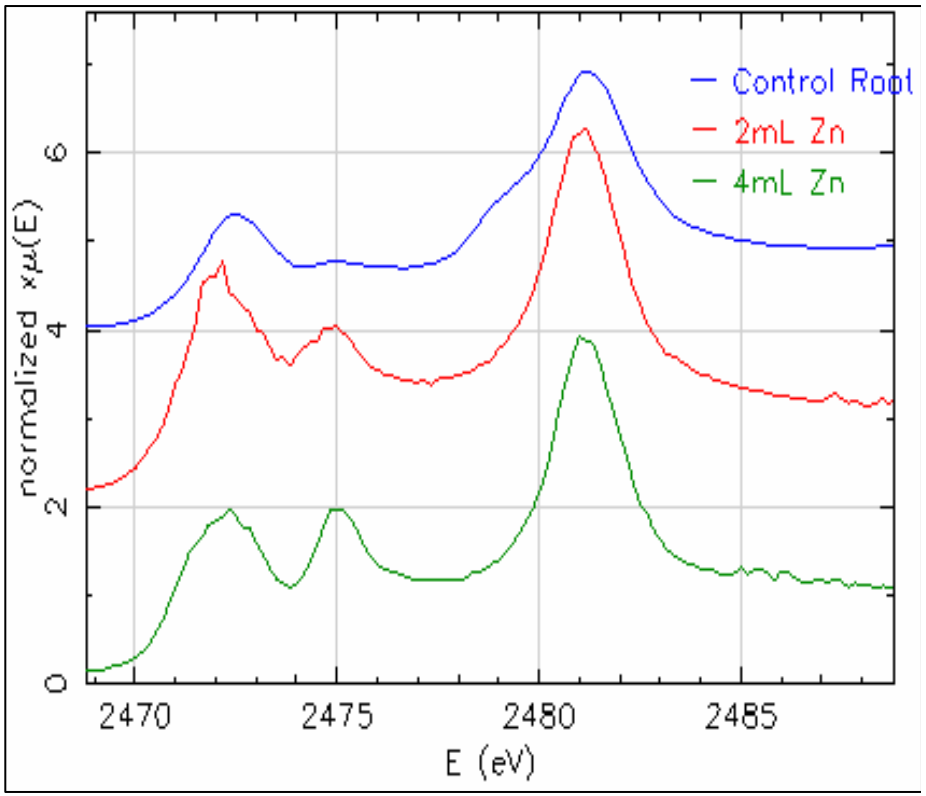


Organic S species

- Sulfur in sediments
- Sulfate (bio)reduction



- Sulfur in plant roots
- Physiological response to toxin (Zn)

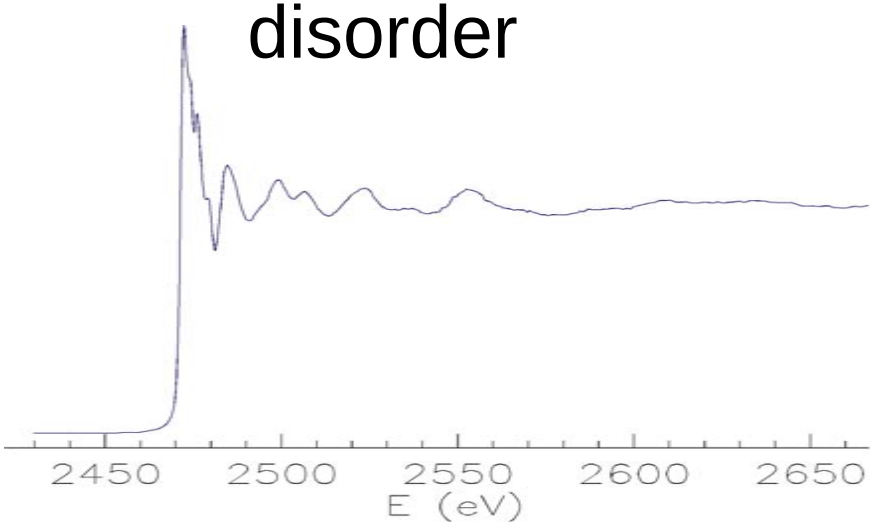


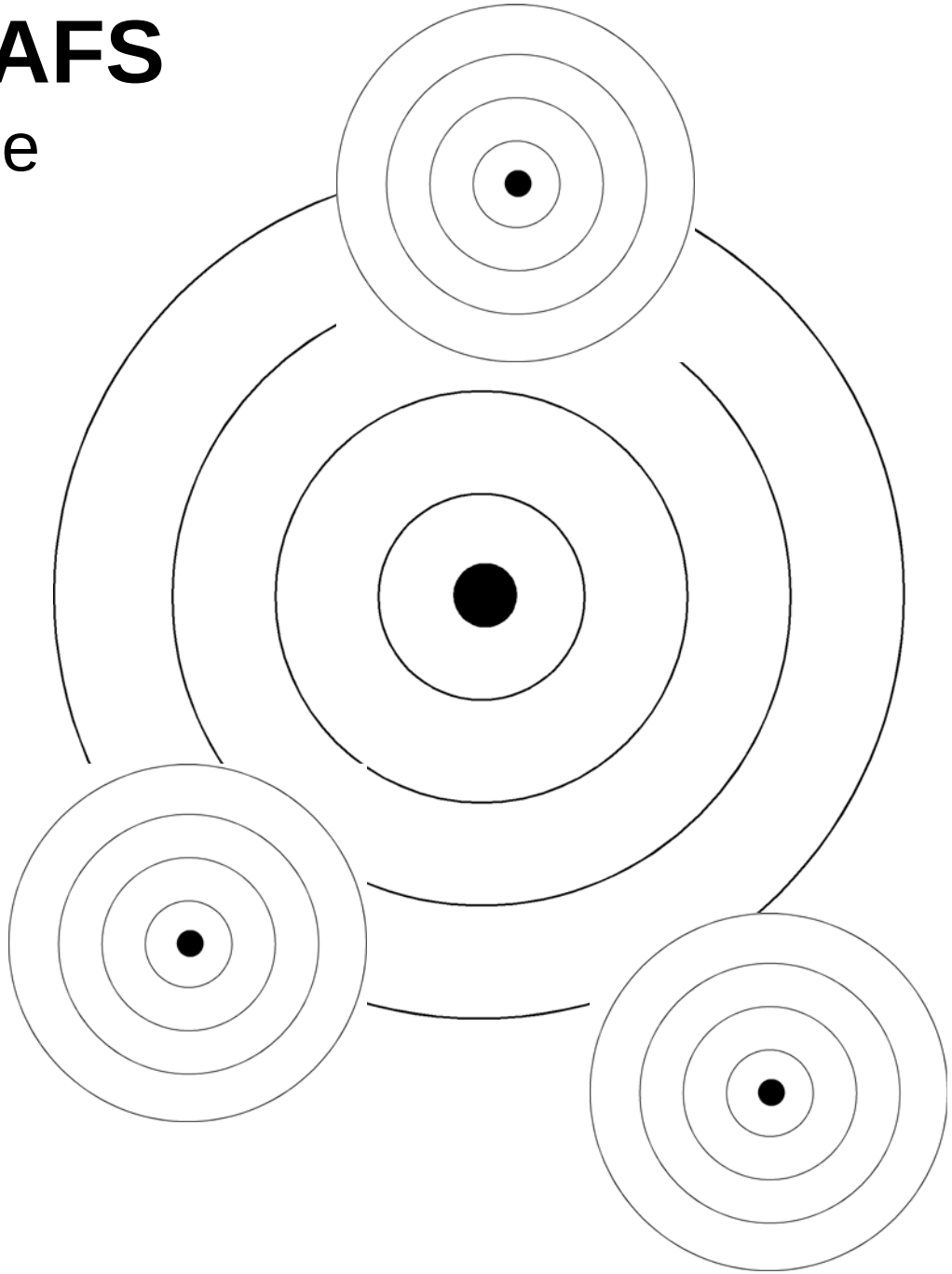
“Soft” X-rays:

- C, N, O edges, very low energy
- Spectral analysis is used to image distribution of different organic compounds and oxides

EXAFS

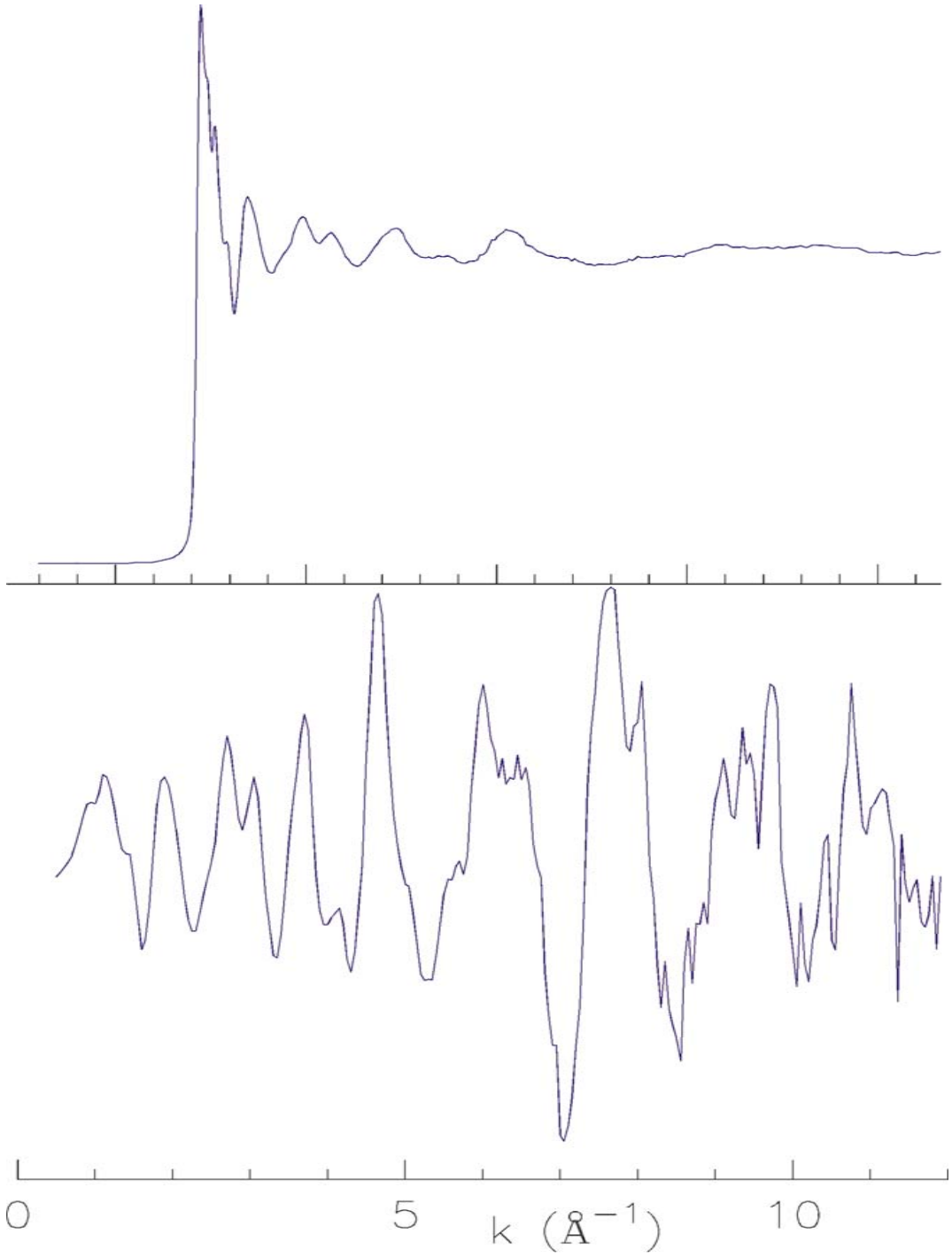
- Extended oscillations due to backscatter of electron from neighboring atoms
- Interference pattern:
- Distance
- What element (size)
- Coordination number
- positional/vibrational disorder





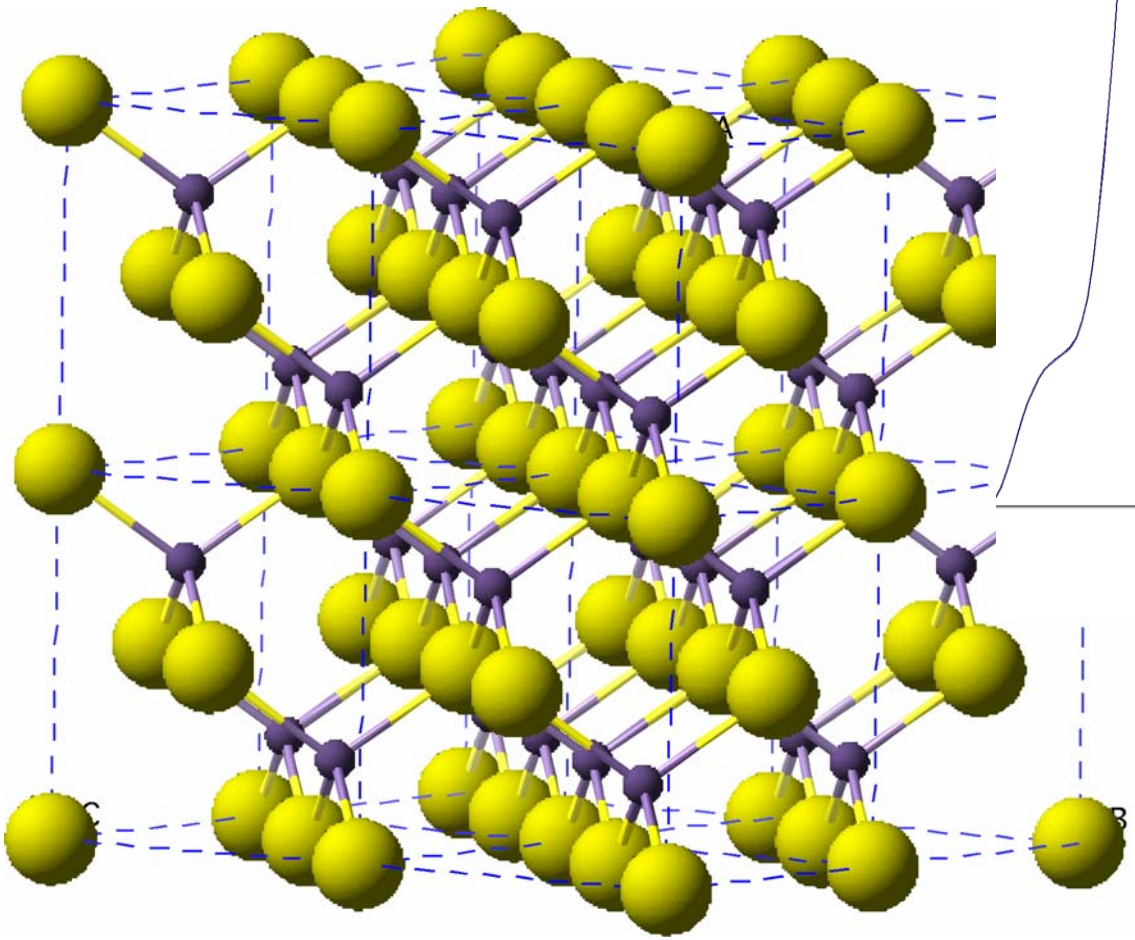
EXAFS data analysis

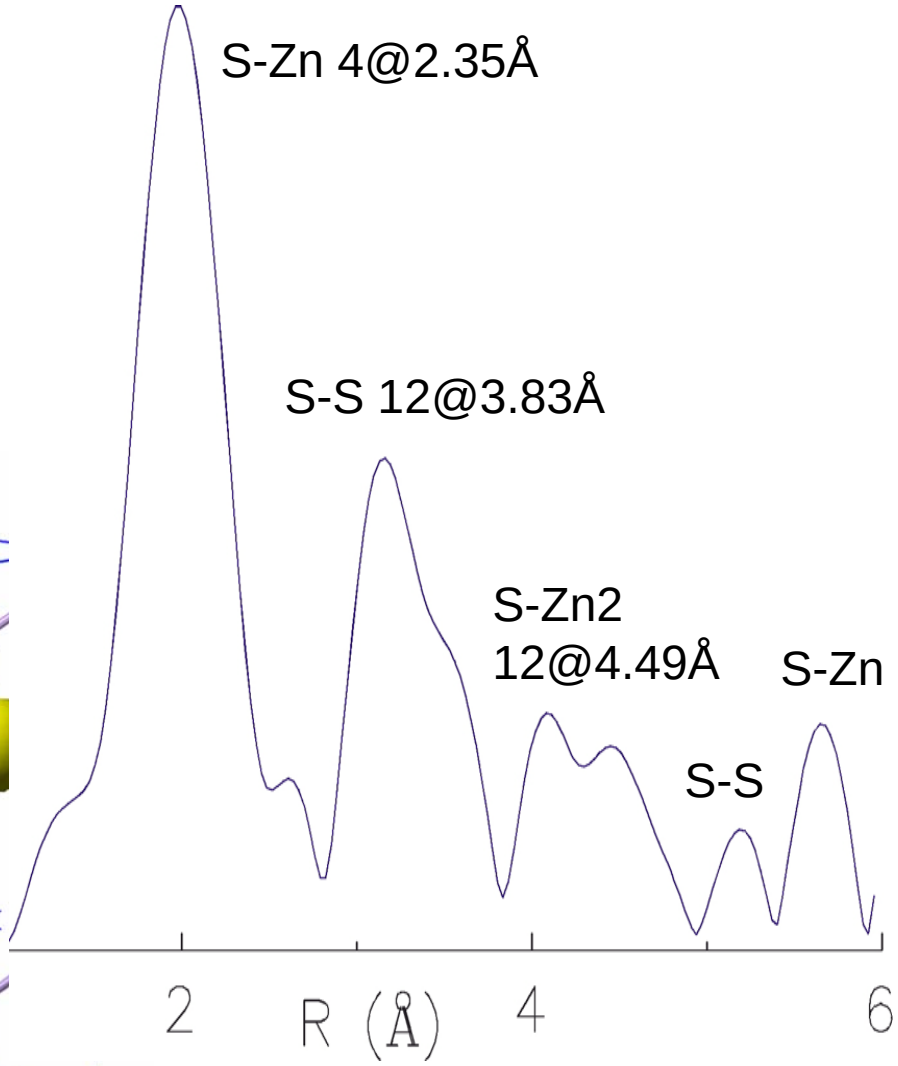
- Example: S in ZnS
- Convert to frequency (not linear with energy)
- Fourier transform to resolve multiple frequencies



EXAFS data analysis

S in ZnS structure

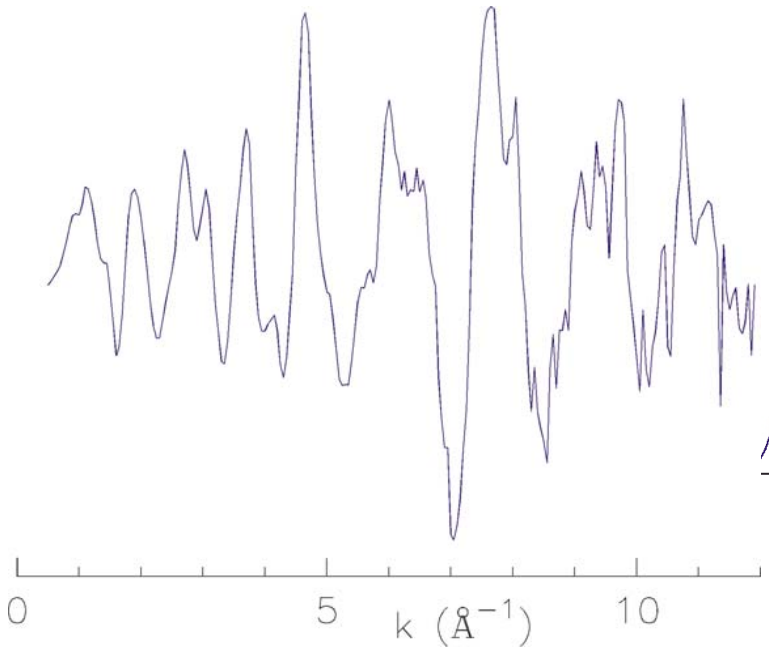


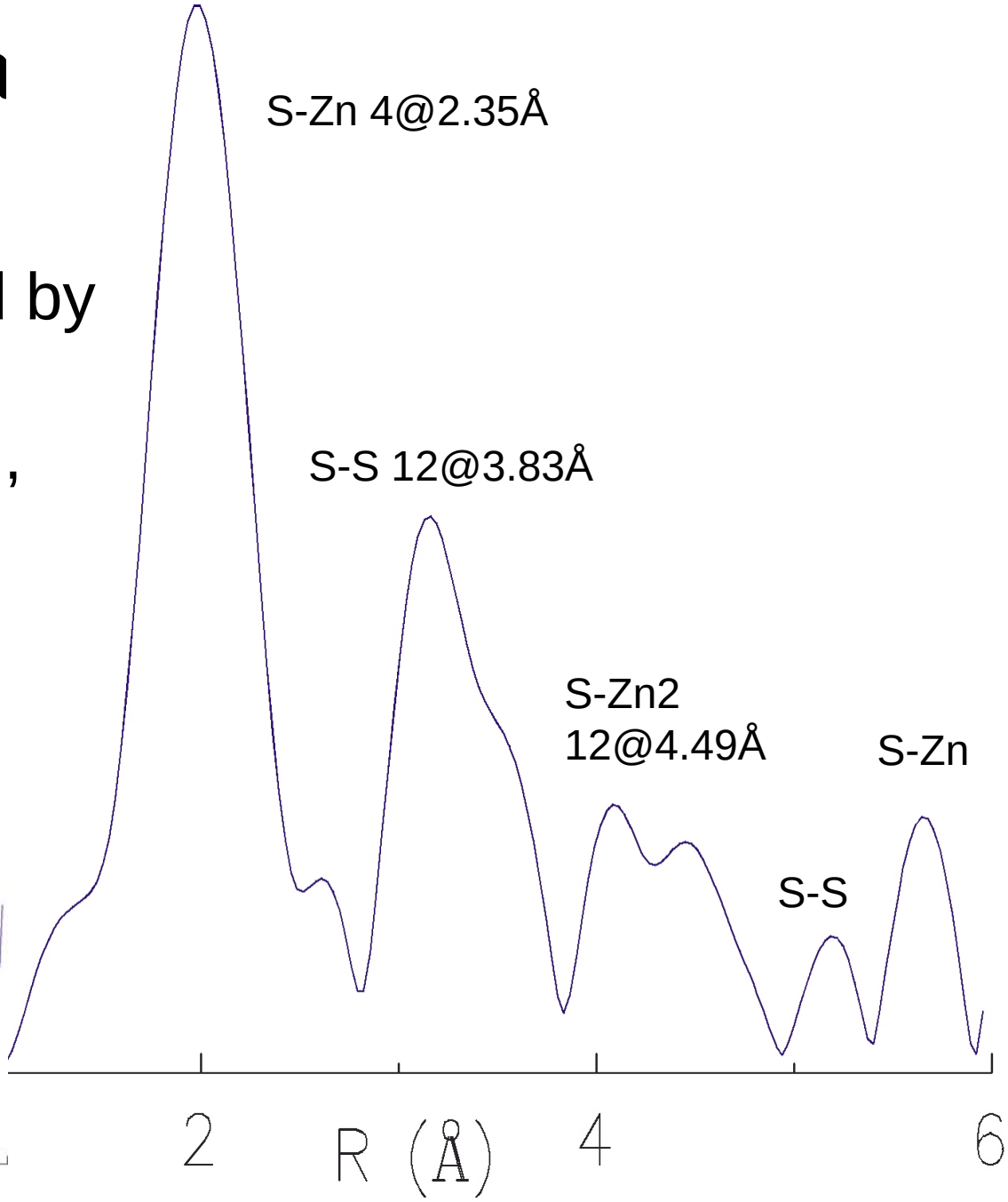


Fourier transform

EXAFS data analysis

- Results are obtained by fitting a model to data
- 1D radial distribution, not 3D structure
- Short range





Limitations

- General:
  - Complexity of spectrum -- all components superimposed
  - Complexity of sample -- shows “Average” configuration
  - Experimental challenges -- sample prep & preservation, energy ranges, interferences, etc.
- EXAFS:
  - requires single species
  - needs greater energy range & concentration
  - fits a model -- model must be close
  - easily abused by over-interpretation